



Designation: C791 – 11

Standard Test Methods for Chemical, Mass Spectrometric, and Spectrochemical Analysis of Nuclear-Grade Boron Carbide¹

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1. Scope

1.1 These test methods cover procedures for the chemical, mass spectrometric, and spectrochemical analysis of nuclear-grade boron carbide powder and pellets to determine compliance with specifications.

1.2 The analytical procedures appear in the following order:

	Sections
Total Carbon by Combustion in an Inductive Furnace and Infrared Measurement	7-16
Total Boron by Titrimetry and ICP OES	17-27
Isotopic Composition by Mass Spectrometry	28-32
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Chloride and Fluoride by Ion-Selective Electrode	50-58
Water by Constant-Voltage Coulometry and Weight Loss on Drying	59-62
Metallic Impurities	63 and 64
Soluble Boron by Titrimetry and ICP OES	65-79
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2. Referenced Documents

2.1 *ASTM Standards*:²

C750 Specification for Nuclear-Grade Boron Carbide Powder

C751 Specification for Nuclear-Grade Boron Carbide Pellets

D1193 Specification for Reagent Water

3. Significance and Use

3.1 Boron carbide is used as a control material in nuclear reactors. In order to be suitable for this purpose, the material must meet certain criteria for assay, isotopic composition, and impurity content. These methods are designed to show whether

¹ These test methods are under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and are the direct responsibility of Subcommittee C26.03 on Neutron Absorber Materials Specifications.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

or not a given material meets the specifications for these items as described in Specifications **C750** and **C751**.

3.1.1 An assay is performed to determine whether the material has the specified boron content.

3.1.2 Determination of the isotopic content of the boron is made to establish whether the content is in compliance with the purchaser's specifications.

3.1.3 Impurity content is determined to ensure that the maximum concentration limit of certain impurity elements is not exceeded.

4. Reagents

4.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.³ Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

4.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to Specification **D1193**.

5. Safety Precautions

5.1 Many laboratories have established safety regulations governing the use of hazardous chemicals and equipment. The users of these methods should be familiar with such safety practices.

6. Sampling

6.1 Criteria for sampling this material are given in Specifications **C750** and **C751**.

³ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K. and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

TOTAL CARBON BY COMBUSTION IN AN INDUCTIVE FURNACE AND INFRARED MEASUREMENT

7. Scope

7.1 This method covers the determination of total carbon in nuclear-grade boron carbide in either powder or pellet form.

8. Summary of Test Method

8.1 The sample and added combustion accelerators (mostly tungsten-and iron-granules) are heated in an inductive furnace under oxygen atmosphere. The high-frequency field of the furnace couples with electrically conductive components of sample and combustion accelerators. The sample is heated to temperatures not lower than 1400°C and the total carbon content of the sample is released as carbon dioxide and, partially, as carbon monoxide. The reaction gas is passed through a gas-treatment train to ensure that any carbon monoxide formed is converted to carbon dioxide and to remove dust and moisture. The reaction gas is then transferred to the infrared absorption cell of the analyzer. The molecular absorption of carbon dioxide is measured by using a narrow-band optical filter which is translucent for the wavelength of the characteristic infrared absorption of carbon dioxide. The mass fraction of carbon dioxide in the reaction gas is proportional to peak-area of the transient absorption signal. The mass fraction of carbon in the sample is calculated by using a calibration function established by suitable calibration standards measured under comparable conditions.

9. Interferences

9.1 At the specification limits usually established for nuclear-grade boron carbide, interferences are insignificant.

10. Apparatus

10.1 Commonly used laboratory equipment and special equipment according to the following:

10.1.1 *Carbon analyzer*, with induction furnace and infrared absorption cell, suitable to correctly determine the mass fraction of carbon within the concentration range given by boron carbide.

NOTE 1—The correctness of the analysis result can be proved by using matrix analogous reference materials or by comparing with an independent alternative test method.

10.1.2 *Analytical balance*, capable of reading to the nearest 0.01 mg.

10.1.3 *Ceramic crucible*, for example, mullite or alumina.

10.1.4 *Crucible lid with hole*, for example, mullite or alumina.

11. Reagents

11.1 Reagents of known analytical grade shall be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

11.1.1 *Tungsten granules*

NOTE 2—Depending on the particle size of the material the decomposition of the sample in the furnace may be improved by partially replacing

tungsten granules by tin granules. Tungsten/tin-mixtures are commercially available.

11.1.2 *Iron granules*

11.1.3 *Calibration samples*, with defined carbon content, preferably certified reference materials with composition and carbon content similar to the analyzed material. Also suitable are primary substances preferably carbonates.

11.1.4 *Oxygen*, purity $\geq 99.998\%$ v/v.

11.1.5 *Pneumatic gas*, for example, nitrogen, purity $\geq 99.9\%$ v/v.

12. Sampling and Sample Preparation

12.1 Sampling has to be performed in a way that the sample to be analyzed is representative for the total amount of material. In an unknown drying state the sample has to be dried at $(110 \pm 5)^\circ\text{C}$ to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 3—Drying for 2 h is normally sufficient.

12.2 The sample material must have a particle size of $\leq 150\ \mu\text{m}$ (No. 100 sieve). Inhomogeneous sample material has to be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

13. Calibration

13.1 The calibration has to be performed daily according to the manufacturer's instructions. It has to be ensured that the mass of carbon in the calibration sample and test sample are within the same order of magnitude.

NOTE 4—This is achieved by choosing a suitable calibration substance and adapted weights.

13.2 The calibration has to be done according to Section 14.

14. Procedure

14.1 *Preparation of Analysis*—Ceramic crucibles (10.1.3) and crucible lids (10.1.4) have to be cleaned prior to use by firing in a muffle furnace at 1200°C for 1 h. After that, they have to be stored in a desiccator.

14.2 *Determination of Blank Value (Method Blank)*—The same procedure according to 14.4 has to be applied, however without addition of boron carbide. At least three blanks should be determined at least once in each 8-h shift in which total carbon analyses are made.

14.3 *Conditioning of Carbon Analyzer*—Prior to making the initial analysis, condition the carbon analyzer by performing at least two analysis runs. The same procedure according to section 14.4 has to be applied, however only adding a small amount of boron carbide (that is, a spatula-tip of boron carbide).

14.4 *Determination of Carbon Content*—A sub-sample of 20 to 30 mg of boron carbide powder prepared in accordance to Section 6 is weighed to the nearest 0.01mg into the ceramic crucibles (10.1.3) cleaned according to section 14.1.

NOTE 5—Using modern carbon analysis devices with an automated calculation of the mass fraction of carbon in the sub sample the sample mass has to be entered using the internal or external keyboard. Using

carbon analysis devices which measure the absolute mass of carbon of the sample the sample mass has to be noted for later calculations.

The sample in the crucible is covered with approximately 0.9 g and 1.8 g of iron and tungsten granules (11.1.1 and 11.1.2), respectively. For mixing, the crucible has to be shaken carefully. Afterwards, the crucible is closed with the lid (10.1.4), placed into the induction furnace and the combustion cycle is started. Using modern carbon analysis devices the carbon content is calculated and displayed on the internal or external screen or printed out.

NOTE 6—For the measurement of carbon as main component (B₄C approximately 20 %) carbon analysis devices which collect the formed carbon dioxide in a trap are recommended. By heating the trap the collected carbon dioxide is released and passed to the infrared absorption cell. This leads to a uniform and reproducible release of carbon dioxide and, thus, to an improved repeatability.

Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to Section 14. If necessary, the sample has to be homogenized according to Section 12.

15. Calculation

15.1 The carbon content $w(C_{total})$ of the sample has to be calculated under consideration of sample mass and blank values. The carbon content as mean of the corrected single

values of the multiple determinations shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of carbon as follows:

$$w(C_{total}) = \frac{(m_c - m_{blank}) \times 100}{m_s} \tag{1}$$

where:

- m_c = absolute mass of carbon in the sample, mg,
- m_{blank} = absolute mass of carbon in the blank sample, mg, and
- m_s = sample mass, mg

NOTE 7—Most state of the art analyzers automatically calculate the mass fraction of carbon for each measurement after input of blank values and sample masses.

16. Precision and Bias (1)⁴

NOTE 8—Please see Ref (2) for all precision and bias statements, except those denoted by Ref (3).

16.1 Within the frame of the certification of the boron carbide powder European reference material ERM-ED102, the following precision and bias data was obtained applying the described total carbon method. (See table below.)

⁴The boldface numbers in parentheses refer to the list of references appended to these methods.

Element	Total Carbon Method			ERM-ED102, certified value		Bias of mean of total carbon method to certified value, % (relative)
	Mean, %	Repeatability S _r , %	Reproducibility S _R , %	Mean, %	Uncertainty, %	
C	21.06	0.07	0.25	21.01	0.28	±0.24

TOTAL BORON BY TITRIMETRY AND ICP OES

17. Scope

17.1 This method covers the determination of total boron in samples of boron carbide powder and pellets by titrimetry and ICPOES. The recommended amount of boron for each titration is 100 ± 10 mg.

18. Summary of Method

18.1 Powdered boron carbide is mixed with alkaline reagents and this mixture is fused to decompose the boron carbide. The melt is dissolved in diluted hydrochloric acid and heated or purged with nitrogen to remove carbon dioxide. The boron as boric acid is titrated with standardized sodium hydroxide solution, using the mannitoboric acid procedure (3), (4), and (5). Alternatively, the boron in the samples solution is measured using ICP OES.

NOTE 9—Sodium carbonate or a mixture of sodium carbonate and potassium carbonate (1:1) is normally used as alkaline reagent to decompose the boron carbide.

19. Interferences

19.1 *Titrimetry*—Metallic impurities in high concentrations may distort the inflection points of the titration and should be

precipitated from the sample solution using barium carbonate. No distortion was found for concentrations of Al < 0.2 %, Fe < 2 %, Ti < 1 %. Interferences by dissolved CO₂ shall be removed by heating the sample solution or by purging the sample solution with nitrogen.

19.2 *ICP OES*—Interference effects depend primarily upon the resolving power of the spectrometer and the selection of the analytical lines. In practice, line interferences (spectral interferences) and non spectral interferences are critical. Non-spectral interferences are caused primarily by different chemical composition of calibration solution and sample solution, resulting in an alteration of nebulization and excitation properties. Also, memory-effects can play a role. The best way to minimize non-spectral interferences is the use of calibration samples with the same composition of matrix, ideally certified reference materials.

20. Apparatus

20.1 Commonly used laboratory equipment and special equipment according to the following:

- 20.1.1 *Balance*, analytical, capable of reading to the nearest 0.01 mg.
- 20.1.2 *Burner*, bunsen type.
- 20.1.3 *Hand torch*, with gas-cartridge.

20.1.4 *Filter Paper*, open-textured, very rapid filtering, for coarse and gelatinous precipitates.

20.1.5 *Muffle Furnace*, with temperature programmer and controllable to $\pm 20^\circ\text{C}$ between 700°C and 900°C .

20.1.6 *pH Meter*.

20.1.7 *Platinum Crucible*, 30-mL, standard form with close-fitting cover.

20.1.8 *Titration system*, consisting of:

- (1) pH-electrode
- (2) dosage apparatus for liquids with a resolution of $10\ \mu\text{l}$
- (3) stirrer
- (4) unit for recording the titration curve

20.1.9 *Sequential or Simultaneous Optical Emission Spectrometer with Inductively Coupled Plasma*, suited to measure in a wavelength region of 180 nm to 400 nm, preferably with freely definable background measuring points.

21. Reagents

21.1 Water complying Grade 2 of Specification **D1193** and reagents of known analytical grade shall be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. Store reagents in plastic containers.

21.1.1 *Barium Carbonate*, BaCO_3 .

21.1.2 *Hydrochloric Acid*, HCl , concentrated (sp gr 1.19), *c* (HCl) approximately 10 mol/L.

21.1.3 *Hydrochloric Acid*, HCl , 1:1, *c* (HCl) approximately 5 mol/L.

21.1.4 *Mannitol or Mannitol Solution*, $\text{C}_6\text{H}_{14}\text{O}_6$, with a concentration of 100 g/L.

21.1.5 *pH Buffer Solutions*, for example, with a pH of 4.0, 7.0, 9.0.

21.1.6 *Primary Substances for Determination of Molarity of NaOH Solution*, for example, potassiumhydrogenphthalate or boric acid (NBS SRM 951 or its replacement).

21.1.7 *Potassium Nitrate*, KNO_3 .

21.1.8 *Sodium Carbonate*, Na_2CO_3 , dried at 200°C for 1 h.

21.1.9 *Sodium/Potassium Carbonate Mixture*, $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ 1:1 m/m, dried at 200°C for 1 h.

21.1.10 *Sodium Hydroxide Solution*, NaOH , *c*(NaOH) = 0.1 mol/L. This solution must be carbonate-free.

21.1.11 *Sodium Hydroxide Solution*, NaOH , with a concentration of 200 g/L.

21.1.12 *Nitrogen*, purity $\geq 99.99\%$ v/v.

22. Precautions

22.1 Consideration should be given to boron contamination that can come from reagents, glassware, and perhaps from other sources. If care is used in procuring reagents and if low-boron glassware is used, boron contamination should be negligible. The periodic determination of a blank to check for boron contamination is advisable, particularly whenever a new bottle of any reagent is used.

23. Sampling and Sample Preparation

23.1 Sampling has to be performed in a way that the sample to be analyzed is representative for the total amount of material. In an unknown drying state the sample has to be dried

at $(110 \pm 5)^\circ\text{C}$ to constant weight. The sample is cooled down to ambient temperature in a desiccator and stored therein.

NOTE 10—Drying for 2 h is normally sufficient.

The sample material must have a particle size of $\leq 50\ \mu\text{m}$ (No. 100 sieve). Inhomogeneous sample material has to be homogenized. Standard apparatus and procedures for crushing, milling and homogenization may be used provided that no contamination occurs which lessens the accuracy of the determination.

24. Procedure

24.1 *Preparation of Analysis*—A sub-sample of 100 mg of boron carbide powder prepared in accordance to Section 23 is weighed to the nearest 0.01 mg into the platinum crucible and mixed with approximately 3 g $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ using a microspatula. The mixture is covered with approximately 2 g $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ and the platinum lid is placed on the crucible. Continue with fusion procedures 24.2 or 24.3.

NOTE 11—Instead of sodium/potassium carbonate mixture, sodium carbonate can also be used for boron carbide decomposition.

24.2 Muffle furnace/Bunsen burner fusion procedure:

24.2.1 *Using $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$* —Put the crucible in the muffle furnace. Heat the furnace to 750°C in 2 h and hold this temperature for 4 h. Remove the crucible and let it cool to room temperature.

24.2.2 *Using Na_2CO_3* —Put the crucible in the muffle furnace. Heat the furnace to 600°C in 1 h and then to 750°C in 1 h and then to 900°C in 1.5 h. Hold this temperature for 0.5 h. Remove the crucible and let it cool to room temperature.

24.2.3 Add 20 mg to 30 mg of KNO_3 and heat the closed crucible with a full Bunsen flame until a clear melt is obtained (approximately 2 min). Simultaneously heat the upper part of crucible and lid with the full flame of a hand torch. Allow the melt to cool down to room temperature. If a clear melt is not obtained, repeat procedure 24.2.3. Continue with 24.4.

24.3 *Bunsen Burner Fusion Procedure*—If this fusion technique is used, KNO_3 is not needed. Place a lid on the crucible and heat with a low flame of a Bunsen burner for 15 min. Continue heating for another 75 min while gradually increasing the temperature of the flame until the mixture is completely molten. Continue heating with a full Bunsen flame until decomposition of the boron carbide is completed. Most samples require heating with a full Bunsen flame for about 20 min for complete decomposition. Simultaneously heat the upper part of crucible and lid with the full flame of a hand torch. Allow the melt to cool to room temperature. Continue with 24.4.

NOTE 12—Procedure 24.3 works with both $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ and Na_2CO_3 .

If fusion procedures 24.2 and 24.3 are applied to very fine grained (sub-micron) boron carbide powders lower results for total boron may be obtained. If this is the case, instead of procedures 24.2 and 24.3 the following modified Bunsen burner procedure has to be applied:

Use $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ for sample decomposition. Heat the mixture in the platinum crucible carefully with a low flame just above the melting point of $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ and hold this

temperature until, after a few minutes, a clear melt is obtained. Continue with section 24.4.

24.4 *Dissolution Procedure*—Place crucible and lid in a beaker. Add 50 ml of hydrochloric acid (21.1.3). Swirl the beaker carefully to ensure that the whole surface of crucible and lid is wetted. To accelerate the leaching procedure the solution may be gently heated. To avoid losses of boric acid, the beaker must be covered with a watch-glass. After the melt is completely dissolved, rinse the watch-glass with water into the beaker. Remove crucible and lid from the beaker; rinse both carefully with water, adding the rinses to the beaker. Transfer the solution in the beaker to a 250 ml volumetric flask and rinse the beaker thoroughly with water into the volumetric flask. After this, the volumetric flask is filled up to volume with water. This solution is either used for titrimetric (Section 25) or ICP OES (Section 26) determination of boron or, if required, for barium carbonate precipitation (24.5).

24.5 *Barium Carbonate Separation*—Pipet a 50 ml aliquot of the sample solution obtained by procedure 24.4 into a beaker. To ensure reproducible starting conditions and to reduce the consumption of barium carbonate the solution in the beaker is neutralized with NaOH solution (21.1.11) using a pH meter. Add 1.5 ml of hydrochloric acid (21.1.2). Stir the solution and add barium carbonate until an excess of barium carbonate is visible. Cover the beaker with a watch-glass and bring to a boil for 5 min. Let the precipitate digest for 30 min at 50°C to 60°C (for example, using a sand-bath). Allow the suspension to cool down to room temperature. Rinse the watch-glass with water into the beaker. Separate the precipitate by filtration through an open-textured filter paper and collect the filtrate in a beaker. Rinse the filter paper and precipitate thoroughly four to six times with water and collect the rinses with the filtrate. Set the pH to 2.5 to 3 with hydrochloric acid (21.1.3) and bring to a boil for 2 min (or purge with nitrogen for 10 min) to remove CO₂. Continue with section 25.2.

25. Titrimetric Determination of Boron

25.1 Preparation of Analysis:

25.1.1 Pipet a 50 ml aliquot of the sample solution obtained by procedure 24.4 into a beaker. Fill up with water to a volume of approximately 200 ml. Set the pH to 2.5 to 3 with hydrochloric acid (21.1.3) and bring to a boil for 2 min (or purge with nitrogen for 10 min) to remove CO₂.

25.2 Titration:

25.2.1 Using the titration-system, the solution is titrated to the first inflection point with 0.1 mol/L NaOH (21.1.10). Then 35 ml of a mannitol-solution (21.1.4) or 4 g of solid mannitol is added and finally titrated with 0.1 mol/L NaOH to the second inflection point. The consumption of 0.1 mol/L NaOH between the two inflection points corresponds to the mass of boric acid, respectively boron (titration example see 25.3). To avoid interferences by CO₂ the sample solution must be purged with nitrogen during titration.

NOTE 13—If the inflection point on the titration curve is distorted or if there are multiple inflections that are severe enough to prevent a clear determination of the end point, carbonate or hydrolyzable metals are probably present. The best procedure at this point is to start the analysis over with a new sample. The titrated solution can be salvaged, however, by adjusting the pH to 3.0 with dilute acid and then following the barium

carbonate separation procedure (24.5). Once mannitol has been added at 25.2, the titrated solution can not be salvaged and a new sample must be started.

25.2.2 Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to Sections 24 and 25. If necessary, the sample has to be homogenized according to Section 23. The method blank has to be determined applying the same procedure as described in Sections 24 and 25 (without and with barium carbonate precipitation), however, without addition of boron carbide. If a measurable method blank is detected the single values have to be corrected by the method blank.

25.3 Example of Boron Titration via Mannitoboric Acid: (See Fig. 1.)

25.3.1 The titration curve on the left shows the pretitration, starting at pH 2.75. The first inflection point is at pH 5.76. The titration is continued to pH 8.50. After that, mannitol is added. After waiting until the pH has stabilized (pH 5.65) the main-titration is started. The second inflection point is at pH 8.45. The consumption of 0.1 mol/L NaOH between the two inflection points corresponds to the mass of boric acid, respectively boron.

25.4 Calibration:

25.4.1 Before a measurement series the pH calibration of the titration system has to be performed according to the manufacturer's instructions using pH buffer solutions (21.1.5). For the NaOH solution used for titration the correct molarity has to be determined. For this purpose, preferably solutions of primary substances, for example, potassiumhydrogenphthalate or boric acid (21.1.6), must be titrated with the NaOH solution. The method for total boron determination can be checked through analysis of certified boron carbide reference materials. The bias to the certified boron content can be used to derive a method correction factor which improves the accuracy of total boron determination.

NOTE 14—See Annex A for commercial reference materials.

25.5 Calculation:

25.5.1 The total boron content $w(B_{total})$ of the sample has to be calculated under consideration of sample mass and blank values. The boron content as mean of the corrected single values of the multiple determinations shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of boron as follows:

$$w(B_{total}) = \frac{V_{NaOH} \times F \times V_S \times q \times 100}{V_A \times m_E} \quad (2)$$

$$F = \frac{M_{meas}}{M_{nom}} \quad (3)$$

where:

V_{NaOH} = consumption of 0.1 mol/L NaOH, ml,
 V_S = volume of sample solution, ml,
 V_A = volume of titrated aliquot, ml,
 F = titration correction factor for NaOH,

- M_{meas} = measured molarity of NaOH used for titration, mol/L,
 M_{nom} = nominal molarity of NaOH used for titration, mol/L,
 q = titrimetric factor (see Note 15), and
 m_E = sample mass, mg

NOTE 15— $q = 1.0811$ mg boron per ml 0.1 mol/L NaOH solution, for a natural $^{10}\text{B}/^{11}\text{B}$ isotopic ratio.

25.6 *Precision and Bias*—Within the frame of the certification of the boron carbide powder European reference material ERM-ED102, the following precision and bias data was obtained applying the described titrimetric total boron method. (See table below.)

Element	Titrimetric total Boron Method			ERM-ED102, certified value		Bias of mean of titrimetric total boron method to certified value, % (relative)
	Mean, %	Repeatability S_r , %	Reproducibility S_R , %	Mean, %	Uncertainty, %	
B	78.42	0.13	0.34	78.47	0.31	-0.06

26. ICP OES

26.1 *General Comments*—The sample solution obtained in 24.4 is analyzed for boron using ICP OES. The analysis of sample solutions by ICP OES is well known and comprehensively described in numerous standard test methods. Therefore, a detailed description of the procedure for the analysis of the sample solution by ICP OES is not part of this standard test method. Only information specific to the determination of total boron is given. A precise determination of main components with ICP OES is challenging but possible. However, in routine analysis a lower precision compared to the titrimetric method can be expected.

26.2 *Preparation of Sample Solution*—Assuming a total boron content of 78 % m/m the sample solution obtained in 24.4 has a boron concentration of approximately 310 mg/L. In addition, it has a quite high salt concentration of 20 g/L $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ or Na_2CO_3 , respectively. It is therefore recommended to dilute the sample solution, preferably by a factor of ten. Pipet 10 ml of the solution obtained in 24.4 in a 100 ml volumetric flask. Fill up to volume with water. This solution is then analyzed by ICP OES.

26.3 *Recommended Wavelength*—Recommended boron emission lines are: 182.591 nm, 208.959 nm, 249.677 nm, 249.773 nm.

26.4 *Matrix Solution*—For preparation of calibration and control solutions, the following matrix solution must be used: Weigh 5 g of $\text{Na}_2\text{CO}_3/\text{K}_2\text{CO}_3$ or Na_2CO_3 (depending on the matrix of solution 24.4) into a 250 ml volumetric flask. Add approximately 100 ml of water and 50 ml of hydrochloric acid (21.1.3) and wait until the carbonate has dissolved. Degas the solution in an ultrasonic bath and fill up to volume with water.

26.5 *Calibration*—Calibration of the ICP OES has to be performed before a measurement series according to the manufacturer's instructions. To achieve a high precision of the measurement a 2-point calibration without zero-point has to be applied. Normally, the boron concentrations of the calibration solutions are selected in a manner that one is above, but nearby, and the second one is below the expected boron concentration of the sample solution. To control the calibration a control solution with a boron concentration between both standard solutions is required. The control solution is also used to detect measurement drift during a measurement series.

NOTE 16—Calibration with more than two points is also possible. Known from experience this, however, leads only to a minor improvement of accuracy. For multi-point calibrations the zero-point should also not be included in the calibration function.

Calibration and control solutions shall be prepared using boron stock standard solutions (for example, 1000 mg/L), boric acid or by decomposition of boron carbide certified reference materials. If boron solution or boric acid is used matrix-matching with the solution described in 26.4 is required.

NOTE 17—Assuming a total boron content around 78 % m/m, preparation of the sample solution according to 26.2 and the use of a 1000 mg/L boron standard solution it is recommended to prepare the following calibration and control solutions:

Calibration solution – low: pipet 10 ml of solution 26.4 and 1.0 ml of boron standard solution into a 100 ml volumetric flask and fill up to volume. Resulting boron concentration: 10 mg/L.

Calibration solution – high: pipet 10 ml of solution 26.4 and 3.5 ml of stock standard solution into a 100 ml volumetric flask and fill up to volume. Resulting boron concentration: 35 mg/L.

Control solution: pipet 10 ml of solution 26.4 and 3 ml of stock standard solution into a 100 ml volumetric flask and fill up to volume. Resulting boron concentration: 30 mg/L.

26.6 *Procedure*—The sample solution obtained in 26.2 is used for measurement. To detect a measurement drift the control solution has to be measured within and at the end of the measurement series. To improve the precision each sample solution has to be measured repeatedly.

NOTE 18—For example: each sample solution of the measurement series is measured with three replicates and the measurement series is repeated three times.

NOTE 19—The precision can be improved if the measurement is carried out using an internal standard.

Each sample has to be analyzed at least two times. If the single values of the double-test are deviating more than a given degree, depending on the repeatability of the method, then the analysis has to be repeated according to Sections 24 and 26. If necessary, the sample has to be homogenized according to Section 23. The method blank has to be determined applying the same procedures as described in Sections 24 and 26, however, without addition of boron carbide. If a measurable method blank is detected, the single values have to be corrected by the method blank.

26.7 *Calculation*—The total boron content $w(B_{total})$ of the sample has to be calculated under consideration of sample

mass, dilution factor and blank values. The boron content as mean of the corrected single values of the multiple determinations shall be expressed in mass fractions in % and rounded off in accordance to the uncertainty of measurement.

Calculate the mass fraction of boron as follows:

$$w(B_{total}) = \frac{C_M \times f \times V_S}{10 \times m_E} \quad (4)$$

where:

C_M = measured boron concentration in sample solution (26.2), corrected by blank value, mg/L,

V_S = volume of solution after sample decomposition (24.4), ml,
 f = dilution factor (see 26.2), and
 m_E = sample mass, mg

27. Precision and Bias

27.1 Within the frame of the certification of the boron carbide powder European reference material ERM-ED102, the following precision and bias data was obtained applying the described ICP OES total boron Method. (See table below.)

Element	ICP OES total Boron Method			ERM-ED102, certified value		Bias of mean of ICP OES total boron method to certified value, % (relative)
	Mean, %	Repeatability S_r , %	Reproducibility S_R , %	Mean, %	Uncertainty, %	
B	78.70	0.61	0.63	78.47	0.31	±0.29

ISOTOPIC COMPOSITION BY MASS SPECTROMETRY

28. Scope

28.1 This method covers the determination of the isotopic composition of boron in nuclear-grade boron carbide, in powder and pellet form, containing natural to highly enriched boron.

29. Summary of Method

29.1 Boron isotopic ratios are measured in boron carbide by thermal ionization mass spectrometry (TIMS) without prior chemical separation of boron. Boron is converted to sodium borate by fusion of the boron carbide with sodium hydroxide or sodium carbonate directly on the tantalum filament of the mass spectrometer. The loaded filament is transferred to the mass spectrometer where boron isotopic ratios are measured using the Na_2BO_2^+ ion. When mixing the boron carbide and sodium hydroxide or sodium carbonate, a Na to B ratio of 1:1 is maintained, which gives a stable ion emission within a few minutes after operational vacuum is attained. There is no apparent bias caused by selective volatilization of ^{10}B (6), (7), (8), (9), (10), (11).

As an alternative method, the boron isotopic ratios are measured in boron carbide by ICP-MS.

30. Interferences

30.1 Impurity elements, at the specification limits usually established for nuclear-grade boron carbide, do not interfere. Strontium is a potential interference and it is an impurity element in the tantalum filament material. At the temperature used to ionize sodium borate, however, the strontium impurity in the filament does not volatilize to cause a high bias at mass 88. This potential interference does not occur in ICP-MS.

31. Isotopic Composition by TIMS

31.1 Apparatus:

31.1.1 *Mass Spectrometer*—Commercial instruments are available that meet or exceed the following requirements:

31.1.1.1 *Source*, thermal ionization using single filaments. A vacuum lock is recommended to maintain source vacuum, which increases sample throughput.

31.1.1.2 *Analyzer*, with a vacuum system capable of producing a resolving power of at least 400 and an abundance sensitivity at mass 100 of at least 20 000. Resolving power is defined as $M/\Delta M$, where ΔM is the width, in atomic mass units, of a peak at mass M at 5 % of its height. Abundance sensitivity is defined as the ratio of total ion current at mass M to its contribution at mass $M-1$.

31.1.1.3 *Detector, Faraday Cup, Electron Multiplier, or Scintillatory Photomultiplier*—Data acquisition can be accomplished by a potentiometric recorder or a pulse counting system.

31.1.2 *Mass Spectrometer Accessories*—The following items are required:

31.1.2.1 *Filaments*, tantalum ribbon, nominally 0.001 in. thick, 0.030 in. wide, with optional V-groove. Filaments should be prepared and stored in a manner to minimize contamination, and they should be cleaned before use.

31.1.2.2 *Forming Jig*, used to form filaments into the configuration required by the mass spectrometer used and to hold the filaments in place for welding.

31.1.2.3 *Spot Welder*, used to weld the filament ribbons to the support posts. Welds should be made carefully to ensure good electrical contact, which is necessary for beam stability.

31.1.2.4 *Sample-Loading Unit*, used to heat filaments to at least 800°C. A system permitting an electrical current to pass through the filament is required.

31.1.3 *Mixer Mill*.⁵

31.1.4 *Plastic Pipet*, 5- μl , with a changeable plastic barrel.⁶ Use a pipet only once and then discard it.

⁵ A Spex Industries mixer mill, Model 5100, has been used for this method.

⁶ A Kimble automatic pipet, No. 56300, with disposable polypropylene tips has been used for this method.

31.1.5 *Plastic Vial and Ball*—12.7-mm (0.5-in.) outside diameter by 25.4-mm (1-in.) long vial and 9.52-mm (0.375-in.) diameter ball.

31.2 *Reagents:*

31.2.1 *Acetone.*

31.2.2 *Distilled Water.*

31.2.3 *Isopropyl Alcohol.*

31.2.4 *Sodium Carbonate (Na₂CO₃) Solution, 0.14 M.*

31.2.5 *Sodium Hydroxide (NaOH)*—Pulverize in stainless steel containers with stainless steel balls in a mixer mill and store in a desiccator.

31.2.6 *Toluene.*

31.3 *Precautions*—Consideration should be given to boron contamination from reagents and other sources. Sources of natural boron contamination can be checked by using NBS¹⁰ B-enriched boric acid (SRM 952) as an internal standard (8).

31.4 *Calibration*—Periodic attention should be given to bias and linearity and to counting dead time when an ion-counting technique is used. These factors should be determined when the mass spectrometer is first used and they should be checked whenever a calibration result is obtained that significantly deviates from the accepted value. These factors should also be checked at intervals of not greater than three months.

31.5 *Procedure:*

31.5.1 *Filament Cleaning*—Filament assemblies are made in accordance with a procedure that is appropriate for the mass spectrometer used.

31.5.1.1 Clean the filament assembly by sequentially dipping it in toluene, isopropyl alcohol, and distilled water.

31.5.1.2 Rinse the assembly twice with acetone.

31.5.1.3 Dry the assembly under a heat lamp.

31.5.2 *Filament Loading*—Steps 31.5.2.1-31.5.2.5 are instructions for fusing the sample with NaOH and 31.5.2.6-31.5.2.9 are instructions for an alternative fusion with Na₂CO₃.

31.5.2.1 Weigh 25 ± 2 mg of sample in powder form and transfer it to a plastic vial.

NOTE 20—For pellet samples, crush to a powder using the procedure in Section 12. Sample materials prepared for other analyses can be used if care is taken to prevent cross contamination between samples, particularly between samples of differing boron isotopic compositions.

NOTE 21—To obtain a representative sample if the original sample is in powdered form, thoroughly blend the bulk sample before taking the 25-mg aliquot.

NOTE 22—A quantitative transfer is not required because isotopic ratios only are being determined.

31.5.2.2 Add 72 ± 2 mg of pulverized NaOH from the desiccator to the vial containing the sample.

31.5.2.3 Add a plastic ball and immediately close the vial.

NOTE 23—Avoid atmospheric moisture pickup; moisture interferes with good mixing.

31.5.2.4 Mix for 1 min on the mixer mill.

31.5.2.5 Transfer about 0.1 mg of the mixture to a filament. Proceed to 31.5.2.10 for the fusion.

31.5.2.6 Weigh 5 ± 0.2 mg of sample in powder form and transfer it to a plastic vial (Note 20).

31.5.2.7 Add 1.25 mL of 0.14 M Na₂CO₃ solution to the vial containing the sample.

31.5.2.8 Slurry the mixture with the tip of a plastic pipet until a uniform suspension is obtained.

31.5.2.9 Transfer about 5 μ l of the slurry to a filament. Proceed to 31.5.2.10 for the fusion.

31.5.2.10 Heat the filament gradually just to the point where the filament glows brightly.

NOTE 24—The bright glow is caused by the exothermic reaction of tantalum with NaOH or Na₂CO₃. The fusion produces sodium borate and the melt tightly adheres to the filament.

31.5.3 *Mass Spectrometric Measurement:*

31.5.3.1 Insert the filament assembly into the mass spectrometer.

31.5.3.2 Evacuate the system to about 5×10^{-7} torr (66 μ Pa).

31.5.3.3 Heat the sample by passing an electrical current through the filament until a stable beam of Na₂BO₂⁺ ions is obtained.

31.5.3.4 Scan the spectrum repeatedly in both directions over the mass range desired until at least nine spectra have been obtained.

31.6 *Calculation*—Determine the boron isotopic composition from the mass spectra recorded. Calculate the 89 to 88 peak height ratio from the average peak heights. Subtract 0.00078 to correct for ¹⁷O. Then correct the ratio for mass bias.

31.7 *Precision and Accuracy:*

31.7.1 *Precision*—For the B-10 isotope, the relative standard deviation is 0.22 atom % at a concentration in the boron of 20 atom percent.

31.7.2 *Bias*—The average percent recovery obtained from the analysis of boron carbide control standards over a two-year period was 100.1 %. Those standards were prepared and certified by LASL (2).

32. Isotopic Composition by ICP MS

32.1 *General Comments*—The determination of isotopic ratios by ICP-MS is nowadays a well known state-of-the-art technique and widely applied to various matrices. Therefore, a detailed description of the procedure for the determination of boron isotopic ratio by ICP-MS is not part of this standard test method. Only information specific to the determination of boron isotopic ratio is given.

32.2 *Summary of Method*—In a first step the boron carbide powder sample is decomposed by pyrohydrolysis to boric acid. A sub-sample of the boric acid obtained according to Section 39 is dissolved in water, acidified and measured by ICP-MS.

32.3 The following has to be considered:

(a) the solution measured by ICP-MS should have a boron and nitric acid concentration of approximately 0.5 mg/L and 1 %, respectively.

(b) check thoroughly for boron contamination originating from glassware, nebulizer and tubing.

(c) a certified boric acid reference material (for example, NBS 951) is used as standard to determine the mass-bias per amu. This apparatus-specific factor is used for correction of the isotopic ratio measurements of the sample solutions. To improve the accuracy standard and sample solutions shall be

measured alternately. For each standard the mass-bias/amu has to be determined and used for correction of the following sample solution.

32.4 *Precision and Bias*—Within the frame of the certification of the boron carbide powder European reference material

ERM-ED102 the following precision and bias data was obtained applying the described ICP MS method for isotopic composition. (See table below.)

Element	Isotopic composition by ICP MS			ERM-ED102, certified value		Bias of mean of isotopic composition by ICP MS to certified value, % (relative)
	Mean, %	Repeatability S _r , %	Reproducibility S _R , %	Mean, %	Uncertainty, %	
¹⁰ B	19.910	0.027	0.031	19.907	0.014	+ 0.016

PYROHYDROLYSIS

33. Scope

33.1 This method covers the separation of up to 100 µg of halides per gram of boron carbide. The separated halides are measured using other methods found in this standard. It also covers the sample preparation for the determination of isotopic composition by ICP MS.

34. Summary of Method

34.1 A stream of moist gas is passed over a mixture of powdered sample and U₃O₈ accelerator heated at 1000 to 1100°C. Alternatively, a stream of moist oxygen is passed over the powdered sample at 1100°C, which requires no accelerators. The pyrohydrolytic reaction releases chloride and fluoride as hydrochloric and hydrofluoric acids, which volatilize and collect in the condensate (12), (13), and (14).

35. Interferences

35.1 Interferences are not expected. The conditions given in this method for pyrohydrolysis must be controlled to ensure complete recovery of the halides.

36. Apparatus

(See Fig. 2.)

36.1 *Flowmeter*, capable of measuring a gas flow of up to 250 mL/min.

36.2 *Water Heating Flask*, in which water is boiled by either a hot plate or immersion heater.

36.3 *Tube Furnace*, capable of maintaining a temperature of 1100°C, having 178 to 305-mm (7 to 12-in.) long by about 32-mm (1.25-in.) diameter heating chamber having the heating element extending to near the furnace ends.

36.4 *Pyrohydrolytic Tube*, fused silica or nickel, 30-mm diameter by about 350 mm long with a 29/42 standard taper (inner) joint on one end. To the opposite end is sealed a hang-down tube with a condenser. The condenser is attached to the hang-down tube 10 mm from the top. The hang-down tube is 6 mm outside diameter and the condenser is 152 mm (6 in.) long, 25-mm outside diameter. The distance that the pyrohydrolytic tube extends outside of the furnace to the hang-down tube is 10 mm. This distance is critical in preventing the formation of a boric acid plug in the top end of the hang-down tube.

36.5 *Sample Boat*, fused silica or nickel with a capacity to hold at least 6 g of U₃O₈ and 2 g of sample.

36.6 *Collection Vessel*, a graduated cylinder or graduated centrifuge tube with a volume of about 25 mL.

36.7 *Mixer Mill*.

37. Reagents

37.1 *Accelerator*, U₃O₈ or sodium tungstate with tungsten trioxide:

37.1.1 U₃O₈, powdered, <1 µg Cl and F. Prepare by air calcining UO₂ at 400°C or by oxidizing uranium metal in the following manner: Slowly air-oxidize the metal starting at 300°C and raising the temperature gradually to 800°C over several days. Then ignite the oxide for 20 min at 1000°C in moist argon (conditions for pyrohydrolysis). These two preparations provide U₃O₈ with satisfactory accelerator characteristics, which are thought to be dependent upon the surface area of the oxide.

37.1.2 *Sodium Tungstate (Na₂WO₄) with Tungsten Trioxide (WO₃)* may be used. Dehydrate 165 g of Na₂WO₄ in a large platinum dish. Transfer the dried material to a mortar, add 116 g of WO₃, and grind the mixture to ensure good mixing. Transfer the mixture into a platinum dish and heat with a burner for 2 h. Cool the melt, transfer the flux to a mortar and grind to a coarse powder. Store the flux in an airtight bottle. Mix about 8 g of flux with each portion of sample to be pyrohydrolyzed.

37.2 *Argon*, purity ≥ 99.99 % v/v.

37.3 *Boric Acid*, powder and a saturated solution in distilled water.

37.4 *Distilled Water*, chloride- and fluoride-free, <0.1 µg/g.

37.5 *Oxygen*, purity ≥ 99.99 % v/v.

38. Precautions

38.1 Care must be taken to avoid chloride and fluoride contamination of reagents and laboratory equipment.

39. Procedure

39.1 Prepare a sample and reagent blank as follows:

39.1.1 Crush pellet samples to a powder using the procedure in Section 12. If the pyrohydrolysis is done with oxygen, continue with 39.1.6.

39.1.2 Line two sample boats with 3 g of U₃O₈.

39.1.3 Weigh 1 to 2 g of powdered sample to ±0.01 g and mix thoroughly with 3 g of U₃O₈ accelerator in a mixer mill.

39.1.4 Quantitatively transfer this mixture to one of the sample boats and spread it uniformly along the length of the boat.

39.1.5 Add 3 g of U_3O_8 accelerator to the second sample boat and spread it uniformly along the length of the boat. Continue with 39.2.

NOTE 25—This second boat, which is used for the measurement of the reagent blank, is taken through 39.2-39.14.

39.1.6 Take two sample boats. Weigh 1 to 2 g of powdered sample to the nearest 0.01 g into one sample boat (Note 25).

39.2 Prepare the pyrohydrolysis apparatus for use as follows:

39.2.1 Turn on the tube furnace and allow it to reach 1000 to 1100°C.

NOTE 26—The furnace can be turned on early to avoid delaying analyses.

NOTE 27—Whatever temperature is used within the above range, the same temperature within $\pm 10^\circ\text{C}$ must be used for both samples and standards.

39.2.2 Turn on the cooling water to the condenser on the pyrohydrolytic tube.

39.2.3 Add distilled water to the water heater and turn on the heater to boil the water.

NOTE 28—Start this step early to avoid delaying analyses.

39.2.4 If an accelerator is used, turn on the argon and adjust its flow to about 190 mL/min. Otherwise, turn on the oxygen and adjust its flow to about 190 mL/min.

39.2.5 Adjust the argon flow and water temperature such that 15 ± 2 mL of condensate is produced in about 20 min of operation.

39.3 Open the pyrohydrolytic tube. For determination of chloride by constant-current coulometry, continue with 39.4 and end with 39.9. For determination of chloride and fluoride by ion-selective electrode, continue with 39.10 and end with 39.14.

39.4 Place a collection vessel containing 2 mL of the saturated boric acid solution and 1.5 g of boric acid into position.

NOTE 29—The tip of the hang-down tube should be at least 10 mm below the surface of the boric acid solution.

39.5 Insert a sample boat into the pyrohydrolytic tube and immediately close the tube.

NOTE 30—The sample boat shall be placed in the center of the hot zone of the furnace.

39.6 Collect 15 ± 2 mL of condensate in about 20 min.

39.7 Remove the collection vessel.

39.8 Open the pyrohydrolytic tube, remove the sample boat, and transfer the spent sample to a waste container.

39.9 Dilute the condensate to 20.0 mL with distilled water and mix thoroughly.

NOTE 31—This solution is used for the determination of chloride by constant-current coulometry.

39.10 Place a collection vessel (50 mL volumetric flask) containing 20 mL of water into position.

NOTE 32—The tip of the hang-down tube should be at least 10 mm below the surface of the water level.

39.11 Insert a sample boat into the pyrohydrolytic tube and immediately close the tube.

NOTE 33—The sample boat shall be placed in the center of the hot zone of the furnace.

39.12 Collect approximately 20 mL of condensate in about 20 min.

39.13 Remove the collection vessel.

NOTE 34—This solution is used for the determination of chloride and fluoride by ion-selective electrode.

39.14 Open the pyrohydrolytic tube, remove the sample boat, and transfer the spent sample to a waste container.

40. Pyrohydrolysis as Sample Preparation Procedure for Isotopic Composition by ICP MS

40.1 Use oxygen as carrier gas.

40.2 Crush pellet samples to a powder using the procedure in Section 12.

40.3 Weigh approximately 2 g of powdered sample into a sample boat.

40.4 Prepare the pyrohydrolysis apparatus according to 39.2.1 and 39.2.3.

40.5 Turn on the oxygen and adjust the heating of water heater and flow-rate of oxygen in a way that approximately 200 mL of condensate is collected in approximately 1.5 h.

40.6 Open the pyrolytic tube.

40.7 Place a 250 mL beaker as collecting vessel into position. The tip of the hang-down tube should be near the bottom of the beaker.

40.8 Insert the sample boat into the pyrohydrolytic tube and immediately close the tube.

40.9 Collect approximately 200 mL of condensate in approximately 1.5 h.

40.10 Remove the beaker and switch off the pyrohydrolysis apparatus.

40.11 Open the pyrohydrolytic tube, remove the sample boat, and transfer the spent sample to a waste container.

40.12 Place the beaker in a drying cabinet and evaporate at 110°C to dryness.

40.13 Scratch out the crystalline residue of boric acid with a plastic spatula and use it for determination of isotopic composition by ICP MS.

CHLORIDE BY CONSTANT-CURRENT COULOMETRY

41. Scope

41.1 This method covers the measurement of chloride after separation from boron carbide by pyrohydrolysis. The lower limit of the method is about 2 μg of chloride per titration.

42. Summary of Method

42.1 The condensate is analyzed for chloride with an automatic chloride titrator that coulometrically generates silver ion to form insoluble silver chloride. The end point is sensed amperometrically and the generating current is stopped automatically at a preset increment of indicator current. Since the rate of generating silver ion is constant, the titration time is proportional to the amount of chloride precipitated (12), (15).